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A correlated ab initio study of linear carbon-chain radicals  $C_nH$   
( $n = 2-7$ )

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# A correlated ab initio study of linear carbon-chain radicals $C_nH$ ( $n = 2-7$ )

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## Abstract

Linear carbon-chain radicals  $C_nH$  for  $n = 2-7$  have been studied with correlation consistent valence and core-valence basis sets and the coupled cluster method RCCSD(T). Equilibrium structures, rotational constants, and dipole moments are reported and compared with available experimental data. The ground state of the even- $n$  series changes from  $^2\Sigma^+$  to  $^2\Pi$  as the chain is extended. For  $C_4H$ , the  $^2\Sigma^+$  state was found to lie only  $72\text{ cm}^{-1}$  below the  $^2\Pi$  state in the estimated complete basis set limit for valence correlation. The  $C_2H^-$  and  $C_3H^-$  anions have also been characterized.

## 1. Introduction

The acetylenic linear carbon-chain radicals  $C_nH$  for  $n = 2$  to 6 have all been detected in the interstellar medium (see citations in Refs. [1–3]), with  $C_2H$  particularly plentiful. As reactive precursors in chain-lengthening astrochemical processes, they and the related cyanopolyynes  $C_nN$  radicals play important roles in the evolution of molecular species within dense interstellar and circumstellar molecular clouds. The members of the odd- $n$  series all have  $^2\Pi$  ground states with characteristically high dipole moments, which make them exceptional candidates for astronomical detection. For the even- $n$  series, there are low-lying states of  $^2\Sigma^+$  and  $^2\Pi$  symmetries, where the  $^2\Sigma^+$  state has a much smaller dipole moment than the  $^2\Pi$  state, though large enough to be de-

tected. The ordering of the states unquestionably changes as the length of the chain grows. There is no dispute that the ground state of  $C_2H$  (ethynyl) is a  $^2\Sigma^+$ , while that of  $C_6H$  (hexatriynyl) is  $^2\Pi$ . However, the ground state of the  $C_4H$  butadiynyl radical lies near the point where the ordering of the two states reverses. The experimental spectra of  $C_4H$  are consistent with a  $^2\Sigma^+$  ground state [4–7], but the state separation has not been measured. Calculations by Horn and Botschwina included in Ref. [7] found the  $^2\Sigma^+$  state to be more stable, while Natterer and Koch [8] asserted that the ground state is of  $^2\Pi$  symmetry. Their work, however, left some points unsettled. Thus one goal of the present study is to reexamine this issue in order to ascertain if the proper ground state assignment has been made for  $C_4H$ , as well as to compute accurate values for the state separations of  $C_2H$  and  $C_6H$ .

Although each of the  $C_nH$  species containing up to ten carbon atoms has been the focus of previous ab initio studies, there have been only three efforts to

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characterize all or part of the sequence at the same level of theoretical treatment. Cooper and Murphy [1] reported the results of RHF calculations on the odd- $n$   $C_3H$ ,  $C_5H$ , and  $C_7H$  species using very limited basis sets. Subsequently, Pauzat et al. [3] studied both even- and odd- $n$  radicals from  $C_2H$  through  $C_{10}H$  at the UHF/3-21G and UHF/SVP levels. Finally, the work by Natterer and Koch [8] mentioned above considered the even- $n$  radicals  $C_2H$ ,  $C_4H$  and  $C_6H$ . Only the last paper employed correlated methods. The complete series has not been systematically investigated with correlated methods and robust basis sets. Therefore, the second goal of this work is to study  $C_2H$  through  $C_7H$  with state-of-the-art ab initio theory and substantial basis sets in order to predict molecular properties including structures, rotational constants, and dipole moments.

Finally, the electron affinities (EA) of  $C_2H$  and  $C_3H$ , the two  $C_nH$  species for which experimental values have been measured, were also investigated in this work. The  $C_2H^-$  and  $C_3H^-$  anions are of potential interest in astrochemistry due to their stability and the well-known importance of ion–molecule reactions under astrophysical conditions. Neither EA has received much theoretical attention. In particular,  $C_3H^-$  has only been studied in one previous effort [9], which utilized a moderately-sized basis set (6-31 + + G \* \*) and limited recovery of correlation (CID) but did not report the EA. It did, however, provide the first evidence that the geometry of the ground state of  $C_3H^-$  is not linear and that there is also an intriguing bound excited state. By using larger basis sets and a correlation method [RCCSD(T)] that performs well at describing EAs, we can improve upon earlier predictions.

## 2. Methodology

The correlation consistent basis sets (cc-pVXZ) of Dunning and co-workers [10–12] have been utilized in this work. An extensive series of benchmark calculations [13–18] on small systems have amply demonstrated the well behaved convergence associated with the use of these basis sets, which makes it possible to estimate complete basis set (CBS) limits for various properties when sets of at least double through quadruple zeta quality can be used. Even in

cases where the larger sets cannot be used, there are systematic trends that may be exploited in order to improve the accuracy of the ab initio predictions.

The primary correlation method employed in this study was the restricted coupled-cluster method RCCSD(T) [19] as implemented in the MOLPRO suite of codes<sup>2</sup>. An RHF zeroth-order wave function was used. For the species with  $^2\Pi$  states, the two degenerate components were state-averaged to provide orbitals with the proper symmetry. In order to evaluate the performance of RCCSD(T) for describing the  $^2\Sigma^+ - ^2\Pi$  state separations of the even- $n$  series, internally contracted multireference configuration interaction (CMRCI) calculations [20] were carried out for  $C_2H$  using a complete active space self-consistent field (CASSCF) reference function [21]. The multireference Davidson correction (CMRCI + Q) was also applied [22]. Although most of the correlation calculations were restricted to the valence electrons, the structures of  $C_2H$  and  $C_3H$  were reoptimized with the new cc-pCVTZ set for carbon [12], which includes additional optimized functions located in the core and core–valence region.

Dipole moments at the RCCSD(T) level were determined using the finite field approximation. The basis sets were enlarged to include extra diffuse functions by using the aug-cc-pVXZ sets [11] of double or triple zeta quality.

## 3. Structures, rotational constants, and dipole moments of $C_nH$ species

Optimized equilibrium bond lengths and the associated rotational constants for both even- and odd- $n$   $C_nH$  radicals determined at the RCCSD(T) level of theory are reported in tblr1. The largest valence sets used for each species were dictated by available computational resources. The cc-pVQZ sets were used for the full geometry optimizations of  $C_2H$  and  $C_3H$  and for single-point calculations on  $C_4H$ . The

<sup>2</sup> MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles with contributions by J. Almlöf, R.D. Amos, M.J.O. Deegan, S.T. Elbert, C. Hampel, W. Meyer, K.A. Peterson, R.M. Pitzer, A.J. Stone and P.R. Taylor.

cc-pVTZ sets could be used for C<sub>5</sub>H and single points for C<sub>6</sub>H, while only the cc-pVDZ sets could be used for optimizing C<sub>7</sub>H.

One benefit in examining a large number of species simultaneously is that trends may emerge that are not apparent when examining individual molecules. Here there are a total of 9 C–H and 30 C–C bonds. The latter vary in character from single to triple bonds. When the basis set is improved from cc-pVDZ to cc-pVTZ quality, both C–H and C–C bond lengths decrease, but the effect is remarkably uniform not just for very different C–C bonds, but also for C–C versus C–H bonds. The average ratio ( $r_e(\text{cc-pVTZ})/r_e(\text{cc-pVDZ})$ ) for 6 C–H bonds is 0.9855, but the high–low range is only 0.9853 to 0.9856. The range of 0.9838 to 0.9871 for 13 C–C bonds is larger, but the average is again 0.9855. The predictive power of this parameter for estimating bond lengths at the cc-pVTZ level may be gauged by

considering an example. For C<sub>3</sub>H (<sup>2</sup>Π), the average parameter of 0.9855 produces bond lengths that yield  $B_e = 11.030$  GHz, which is essentially the same as the optimized cc-pVTZ result of 11.028 GHz. If the low and high extremes are used, they lead to respective  $B_e$  values of 11.065 and 10.995 GHz, an interval of only 70 MHz. The average scaling parameter was used to estimate bond lengths for single point cc-pVTZ calculations for the two states of C<sub>6</sub>H in order to produce a more accurate prediction for the state separation (see Section 4).

For the improvement from cc-pVTZ to cc-pVQZ quality, there are only 3 C–H and 4 C–C bond lengths upon which to base scaling factors. Here the average C–H and C–C scaling factors ( $r_e(\text{cc-pVQZ})/r_e(\text{cc-pVTZ})$ ) are somewhat different, 0.9998 for C–H bonds and 0.9970 for C–C bonds. The variation for C–H bonds is again very small, and the range for C–C bonds is only 0.9967 to 0.9978. The

Table 1  
Bond lengths  $r_e$  and rotational constants  $B_e$  for the <sup>2</sup>Σ<sup>+</sup> and <sup>2</sup>Π states of C<sub>*n*</sub>H (*n* = 2–7) at the RCCSD(T) level of theory

Species	State	Basis set	$r_e$ (Å)							$B_e$ (GHz) calc.	$B_0$ (GHz) exp.
			H–C <sub>1</sub>	C <sub>1</sub> –C <sub>2</sub>	C <sub>2</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>4</sub>	C <sub>4</sub> –C <sub>5</sub>	C <sub>5</sub> –C <sub>6</sub>	C <sub>6</sub> –C <sub>7</sub>		
C <sub>2</sub> H	<sup>2</sup> Σ <sup>+</sup>	cc-pVDZ	1.0801	1.2348						42.341	
		cc-pVTZ	1.0645	1.2148						43.723	
		cc-pVQZ	1.0644	1.2108						43.972	
		est. CBS limit	1.0644	1.2088						44.096	43.675
	<sup>2</sup> Π	cc-pVDZ	1.0876	1.3154						37.917	
		est. CBS limit	1.0712	1.2888						39.329	
C <sub>3</sub> H	<sup>2</sup> Π	cc-pVDZ	1.0813	1.2661	1.3670					10.712	
		cc-pVTZ	1.0654	1.2484	1.3468					11.028	
		cc-pVQZ	1.0653	1.2456	1.3426					11.085	
		est. CBS limit	1.0653	1.2443	1.3405					11.112	11.186
		cc-pVDZ	1.0793	1.2334	1.3947	1.2396				4.578	
C <sub>4</sub> H	<sup>2</sup> Σ <sup>+</sup>	cc-pVTZ	1.0635	1.2146	1.3787	1.2200				4.708	
		cc-pVQZ <sup>a</sup>	1.0633	1.2104	1.3744	1.2157				4.738	4.759
		est. CBS limit	1.0645	1.2244	1.3402	1.2942				4.642	
	<sup>2</sup> Π	cc-pVDZ	1.0805	1.2470	1.3621	1.3179				4.484	
		cc-pVTZ	1.0648	1.2286	1.3444	1.2984				4.612	
		cc-pVQZ <sup>a</sup>	1.0645	1.2244	1.3402	1.2942				4.642	
C <sub>5</sub> H	<sup>2</sup> Π	cc-pVDZ	1.0805	1.2457	1.3567	1.2899	1.3371			2.302	
C <sub>6</sub> H	<sup>2</sup> Σ <sup>+</sup>	cc-pVTZ	1.0648	1.2276	1.3392	1.2727	1.3176			2.366	2.395
		cc-pVDZ	1.0796	1.2349	1.3881	1.2397	1.3880	1.2411		1.339	
	<sup>2</sup> Π	cc-pVTZ <sup>a</sup>	1.0639	1.2171	1.3680	1.2217	1.3679	1.2231		1.379	
		cc-pVDZ	1.0804	1.2389	1.3734	1.2598	1.3462	1.3185		1.332	
C <sub>7</sub> H	<sup>2</sup> Π	cc-pVTZ <sup>a</sup>	1.0648	1.2210	1.3535	1.2415	1.3267	1.2994		1.371	1.386
		cc-pVDZ	1.0804	1.2395	1.3724	1.2608	1.3357	1.2997	1.3288	0.842	

<sup>a</sup> Single-point calculation at geometry derived from smaller set(s) (see text).

two average scaling factors were used to estimate bond lengths in order to run the cc-pVQZ calculations for  $C_4H$  that appear in Table 1 and play an important role in Section 4.

The effect of including core and core–valence correlation can be approximated by running all-electron calculations at the cc-pCVTZ level and observing the changes in bond lengths with respect to valence-electron calculations at the cc-pVTZ level. The structures of  $C_2H$  (both states) and  $C_3H$  were therefore reoptimized. The C–H bonds are essentially unchanged, but the C–C bonds decrease by an average of 0.0034 Å, which is consistent with shifts observed in C–C bonds in  $C_2$  [23],  $C_3$  [24] and MgCCH [25].

Rotational constants are the principle point of comparison between the present calculations and experimental or astronomical data. Measured  $B_0$  values are indicated in Table 1, as collected by Pauzat et al. [3]. Passing over  $C_2H$  for the moment, the agreement is very good between the RCCSD(T) values (valence correlation, CBS limits or largest basis set result) and the empirical data for species where there is no dispute over the ground state assignment. The computed  $B_e$  values for  $C_3H$ ,  $C_5H$  and  $C_6H$  fall only 74, 29 and 57 MHz below the measurements, where some adjustment for zero-point vibrational motion and other theoretical approximations should be expected. The estimated cc-pVQZ geometries for  $C_4H$  yield  $B_e$  values that fall 21 and 117 MHz below the result of Gottlieb et al. [5] for the  $^2\Sigma^+$  and  $^2\Pi$  states, respectively, which offers tentative support for a  $^2\Sigma^+$  ground state. When core–valence contractions of 0.0034 Å per C–C bond are added to the valence CBS limits or best basis set results noted above, the values of  $B_e$  become 11.165, 4.763, 2.379 and 1.384 GHz for the ground states of  $C_3H$  to  $C_6H$ , respectively. The respective errors of 21, 4, 16 and 2 MHz are significantly reduced from the valence-only results.

Theory overestimates  $B_e$  for  $C_2H$  by more than 400 MHz. The RCCSD(T) results were tested against the CMRCI method. The CMRCI estimated CBS limits for the  $^2\Sigma^+$  and  $^2\Pi$  states were found to be 44.003 and 39.372 GHz, respectively, which differ from RCCSD(T) by 93 and 71 MHz. The behavior of the RCCSD(T) method is not anomalous. The large difference between theory and experiment may

Table 2  
Dipole moments  $\mu_e$  of the  $^2\Sigma^+$  and  $^2\Pi$  states of  $C_nH$  at the RCCSD(T) level

Species	Basis set		$\mu_e$ (D)	
	C	H	$^2\Sigma^+$	$^2\Pi$
$C_2H$	cc-pVDZ	cc-pVDZ	0.766	2.829
	aug-cc-pVDZ	cc-pVDZ	0.772	2.965
	aug-cc-pVDZ	aug-cc-pVDZ	0.774	2.968
	cc-pVTZ	cc-pVTZ	0.774	2.960
	aug-cc-pVTZ	cc-pVTZ	0.771	3.006
	aug-cc-pVTZ	aug-cc-pVTZ	0.769	3.004
$C_3H$	aug-cc-pVDZ	cc-pVDZ	–	3.512
	aug-cc-pVTZ	cc-pVTZ	–	3.551
$C_4H$	aug-cc-pVDZ	cc-pVDZ	0.870	4.404
$C_5H$	aug-cc-pVDZ	cc-pVDZ	–	4.881
$C_6H$	aug-cc-pVDZ	cc-pVDZ	0.979	5.536
$C_7H$	aug-cc-pVDZ	cc-pVDZ	–	5.945

be due to the vibration effects incorporated in the latter value. It is noteworthy that  $B_e$  is very sensitive to the C–C bond length: a change of only 0.001 Å shifts  $B_e$  by 60 MHz. In fact, including core and core–valence correlation increases the error by more than 200 MHz.

The RCCSD(T) dipole moments  $\mu_e$  of  $C_nH$  radicals are given in Table 2. It is evident from  $C_2H$  that  $\mu_e$  is significantly changed by adding diffuse functions to C, but not to H. Therefore, this pairing of the aug-cc-pVXZ set for C with the standard cc-pVXZ set for H was used for the larger species as well. Furthermore, the results for  $C_2H$  and  $C_3H$  indicate that there is little to be gained by improving from double to triple zeta quality sets. The impact is negligible for the  $^2\Sigma^+$  state of  $C_2H$  and only about 0.05 D for the  $^2\Pi$  states of  $C_2H$  and  $C_3H$ . The correlated RCCSD(T) values are expected to be somewhat more reliable than the RHF or UHF values reported in previous work [1,3]; unfortunately, there are no experimental values for comparison. It is of interest to note that although the dipole moments of both states increase with chain length, the magnitude doubles for the  $^2\Pi$  state from  $C_2H$  to  $C_7H$ . Of note: although a large dipole moment improves the likelihood of detecting a species, it also increases the long range attraction for other molecules and may lead to rapid destruction of the longer  $C_nH$  radicals that have not been detected.

#### 4. The ${}^2\Sigma^+ - {}^2\Pi$ state separations of $C_2H$ , $C_4H$ , and $C_6H$

The determination of accurate excitation energies requires a balanced treatment of the two states with respect to both methodology and the one-electron basis sets employed. In order to judge the expected accuracy of RCCSD(T)/cc-pVXZ calculations for describing the  ${}^2\Sigma^+ - {}^2\Pi$  equilibrium state separation  $T_e$  of  $C_nH$  species, we will begin by benchmarking the behavior of  $C_2H$ . Although there have been several attempts to measure this quantity, a high accuracy value has not been determined. Values have ranged from 1600 to 3800  $\text{cm}^{-1}$  [25]. The best theoretical work on  $C_2H$  has been reported by Kraemer et al. [26] ( $T_e = 3650 \text{ cm}^{-1}$ ), Koures and Harding [27] ( $T_e = 3550 \text{ cm}^{-1}$ ), Thümmel et al. [28] ( $T_e = 3300 \text{ cm}^{-1}$ ) and Perić et al. [29], which should be consulted for citations to other previous ab initio work.

Table 3 lists total energies and  $T_e$  for CMRCI, CMRCI + Q, and RCCSD(T) calculations on  $C_2H$  with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets and the extrapolation to the CBS limit. Given that it is not unusual to find CMRCI and CMRCI + Q calculations bracketing experiment [30], the intermediate location of the RCCSD(T) result lends credibility to using the method for  $C_4H$  and  $C_6H$ .

Table 3

Total energies  $E_e$  and excitation energy  $T_e$  of the  ${}^2\Sigma^+$  and  ${}^2\Pi$  states of  $C_2H$  at the indicated levels of theory

Method	Basis set	$E_e (E_h)$		$T_e (\text{cm}^{-1})$
		${}^2\Sigma^+$	${}^2\Pi$	
CMRCI	cc-pVDZ	-76.39842	-76.38398	3169.2
	cc-pVTZ	-76.46115	-76.44492	3562.1
	cc-pVQZ	-76.47958	-76.46280	3682.8
	est. CBS limit	-76.48987	-76.47277	3753
CMRCI + Q	cc-pVDZ	-76.40374	-76.39059	2886.1
	cc-pVTZ	-76.46961	-76.45517	3169.2
	cc-pVQZ	-76.48892	-76.47405	3263.6
	est. CBS limit	-76.49969	-76.48458	3316
RCCSD(T)	cc-pVDZ	-76.40063	-76.38738	2908.0
	cc-pVTZ	-76.46779	-76.45301	3243.8
	cc-pVQZ	-76.48763	-76.47236	3351.4
	est. CBS limit	-76.49872	-76.48316	3415
	cc-pCVTZ	-76.569561	-76.554047	3404.9

Table 4

Total energies  $E_e$  and excitation energy  $T_e$  of the  ${}^2\Sigma^+$  (even  $n$ ) and  ${}^2\Pi$  states of  $C_nH$  at the RCCSD(T) level; a positive value of  $T_e$  indicates that the  ${}^2\Sigma^+$  state is more stable

Species	Basis set	$E_e (E_h)$		$T_e (\text{cm}^{-1})$
		${}^2\Sigma^+$	${}^2\Pi$	
$C_3H$	cc-pVDZ	-	-114.35711	
	cc-pVTZ	-	-114.45638	
	cc-pVQZ	-	-114.48575	
	est. CBS limit	-	-114.50216	
$C_4H$	cc-pVDZ	-152.33985	-152.34105	-263
	cc-pVTZ	-152.47463	-152.47487	-53
	cc-pVQZ <sup>a</sup>	-152.50249	-152.50236	29
	est. CBS limit	-152.51664	-152.51631	72
$C_5H$	cc-pVDZ	-	-190.30893	
	cc-pVTZ	-	-190.47665	
$C_6H$	cc-pVDZ	-228.28273	-228.28764	-1078
	cc-pVTZ <sup>a</sup>	-228.48539	-228.48946	-895
$C_7H$	cc-pVDZ	-	-266.25606	

<sup>a</sup> Single point calculation was performed using estimated bond lengths (see text).

The computed total energies for  $C_3H$  through  $C_7H$  as well as the  $T_e$  values for  $C_4H$  and  $C_6H$  are in Table 4. For  $C_4H$ , the most recent correlated calculations for  $T_e$  are the combined experimental and theoretical study reported by McCarthy [7] and the work of Natterer and Koch [8]. Since the former study is quite similar to the present one, this discussion will focus on the latter work. Natterer and Koch found the  ${}^2\Sigma^+$  state to be more stable at the MCSCF and MRCI levels, but the  ${}^2\Pi$  state was more stable at the MRCI + Q, ACPF, and RCCSD(T) levels of theory. For the ACPF and MRCI + Q methods, the  ${}^2\Pi$  state was more stable than the  ${}^2\Sigma^+$  state by 100 to 240  $\text{cm}^{-1}$ , depending upon the basis set used. On the other hand,  $T_e$  jumped to -1137  $\text{cm}^{-1}$  or more for the RCCSD(T) method. The present calculations are at odds with these results. With the smallest cc-pVDZ sets, the  ${}^2\Pi$  state is more stable, but only by 263  $\text{cm}^{-1}$ . Improving the basis sets lowers the  ${}^2\Sigma^+$  state preferentially, and it becomes more stable at the cc-pVQZ level, though only by 29  $\text{cm}^{-1}$ . Extrapolating to the CBS limit stabilizes the  ${}^2\Sigma^+$  state to 72  $\text{cm}^{-1}$  relative to the  ${}^2\Pi$  state. The benchmark calculations on  $C_2H$  suggest that, if anything, RCCSD(T) may be underestimating  $T_e$ . Unfortunately, Natterer and Koch did not report calcula-

tions on the state separation in  $C_2H$ , which would have provided a test on the approach they adopted for  $C_4H$ . Aside from using different basis sets, they also ran the correlated calculations at their MCSCF optimized geometries. Their bond lengths are roughly comparable to the present RCCSD(T)/cc-pVTZ values, so this cannot account for the  $1000\text{ cm}^{-1}$  difference in  $T_e$  at either the cc-pVTZ level.

Natterer and Koch were forced by convergence problems in their RHF and UHF calculations to adopt the quasi-RHF (QRHF) method to generate zeroth-order wave functions. When MOLPRO was used to run an RCCSD(T) calculation based on an RHF wave function with the [4321/321] ANO basis set (yielding respective total energies for the  $^2\Pi$  and  $^2\Sigma^+$  states of  $-152.47037$  and  $-152.46864 E_h$ ), the  $^2\Pi$  state was found to be only  $378\text{ cm}^{-1}$  more stable than the  $^2\Sigma^+$  state, rather than the  $1137\text{ cm}^{-1}$  reported in Ref. [8]. The new value is more consistent with the present results and implies that the QRHF wave function introduces a large amount of error. Also, the MRCI and ACPF results noted above are closer to the RHF-based value of  $T_e$ .

While the cc-pVTZ and [4321/321] ANO sets yield similar total energies, their respective  $T_e$  values differ by more than  $300\text{ cm}^{-1}$ . In order to test the accuracy of the ANO sets for describing state separations, the [4321/321] ANO contraction was used to determine  $T_e$  for  $C_2H$  (again at the cc-pVTZ geometry). A value of  $2785\text{ cm}^{-1}$  was obtained (with total energies for the  $^2\Sigma^+$  and  $^2\Pi$  states of  $-76.46284$  and  $-76.45015 E_h$ ), which is about  $460\text{ cm}^{-1}$  below the cc-pVTZ result and in much poorer agreement with typical theoretical values. The trend for both  $C_2H$  and  $C_4H$  indicates that the [4321/321] ANO set performs less accurately than the cc-pVDZ set. The ANO sets are also much more computationally demanding. The present conclusion that the ground state of  $C_4H$  is a  $^2\Sigma^+$  state is reinforced, although clearly the  $^2\Pi$  state must lie remarkably close.

For  $C_6H$ , previous correlated efforts include the CI work of Pauzat and Ellinger [2], where the  $^2\Pi$  state was found to be more stable than the  $^2\Sigma^+$  state by  $6385$  and  $2379\text{ cm}^{-1}$  in first-order (FOCI) and limited second-order (SOCl) calculations, respectively. Natterer and Koch [8] reported a state separation of  $2175\text{ cm}^{-1}$  at the QRHF + CCSD(T)/

[4321/321] level. The best present value, using the cc-pVTZ sets and estimated geometries, places the  $^2\Pi$  state  $895\text{ cm}^{-1}$  below the  $^2\Sigma^+$  state.

Core and core–valence correlation impact excitation energies as well as bond lengths. Table 3 shows that the  $^2\Sigma^+$  state of  $C_2H$  is stabilized by an additional  $160\text{ cm}^{-1}$  with respect to the valence-electron triple zeta result when the cc-pCVTZ sets were used in all-electron calculations. If the trend observed in  $CH_2$  [12] carries over to  $C_2H$ , this correction may be too small by about 50% with respect to the CVXZ limit. The shift in  $C_2H$  suggests that the state separation in  $C_4H$  may be somewhat larger than the  $< 100\text{ cm}^{-1}$  valence CBS limit, perhaps reaching the  $200\text{--}300\text{ cm}^{-1}$  range.

## 5. Electron affinities of $C_2H$ and $C_3H$

The electron affinities of  $C_2H$  and  $C_3H$  were computed at the RCCSD(T) level by optimizing  $C_2H^-$  and  $C_3H^-$  with the aug-cc-pVTZ set on C and the cc-pVTZ set on H, which required reoptimizing the neutrals with the same sets. Geometries, energies and EAs are presented in Table 5. This strategy was sufficient to reproduce the EA of  $C_2H$  to within the experimental uncertainty ( $2.969 \pm 0.006\text{ eV}$ , [31]), although the inclusion of a partial zero-

Table 5  
Structures ( $r_e$ , Å; angle, deg) and total energies ( $E_e$ ,  $E_0$ ,  $E_h$ ) of  $C_2H$ ,  $C_3H$  and their anions and adiabatic electron affinities (EA, eV) at the RCCSD(T)/(C: aug-cc-pVTZ; H: cc-pVTZ) level; experimental values are  $C_2H$  ( $2.969 \pm 0.006$ ) and  $C_3H$  ( $1.858 \pm 0.023$ )

Species	Quantity	Neutral	Anion
$C_2H$	$r_e$ ( $C_1\text{--}C_2$ )	1.2152	1.2549
	$r_e$ ( $C_2\text{--}H$ )	1.0658	1.0726
	$E_e$	-76.47122	-76.58015
	(EA) <sub>e</sub>	2.964	
	$E_0$	-76.45727	-76.56592
	(EA) <sub>0</sub>	2.957	
$C_3H$	$r_e$ ( $C_1\text{--}C_2$ )	1.3468	1.2897
	$r_e$ ( $C_2\text{--}C_3$ )	1.2484	1.3605
	$r_e$ ( $C_3\text{--}H$ )	1.0654	1.1142
	$\angle$ ( $C_1\text{--}C_2\text{--}C_3$ )	180	174.73
	$\angle$ ( $C_2\text{--}C_3\text{--}H$ )	180	-108.25
	$E_e$	-114.46241	-114.52949
	(EA) <sub>e</sub>	1.825	

point correction (omitting the frequencies associated with the Renner–Teller split bending modes) increases the error slightly, to 0.012 eV. Values of 3.15 and 2.96 eV, computed by Lima and Canuto [32] and Natterer and Koch [8], respectively, have previously been reported. Both C–C and C–H bonds length increase slightly in the anion, a  $^1\Sigma^+$  state, but the effect is larger ( $\approx 0.04$  Å) for the C–C bond.

While  $C_2H^-$  is linear,  $C_3H^-$  is not. The ground state is of  $^1A'$  symmetry, and there is a low-lying, bound excited state of  $^3A''$  symmetry. For the  $^1A'$  state, the C–C–C angle remains quasilinear ( $\approx 175^\circ$ ), but the C–C–H angle has decreased to  $141.2^\circ$ . The C–C–H dihedral angle is  $180^\circ$ , making the terminal C and H *trans* with respect to the central C pair. The two C–C bond lengths change significantly with respect to the neutral. The computed equilibrium EA is 1.825 eV, which falls just slightly below the experimental range of  $(1.858 \pm 0.023)$  of Oakes and Ellison [33]. Our result appears to be the first theoretical prediction of this quantity. The  $^3A''$  state ( $E_e = -114.52730 E_h$ ) lies only  $481 \text{ cm}^{-1}$  above the ground state with the triple zeta sets, but its geometry is somewhat different:  $r_e(C_1-C_2) = 1.309$  Å,  $r_e(C_2-C_3) = 1.312$  Å,  $r_e(C_3-H) = 1.076$  Å,  $\angle(C-C-C) = 174.66^\circ$  and  $\angle(C-C-H) = 141.20^\circ$ . Dua et al. [9] reported structures optimized at the HF level for both states that are similar to the RCCSD(T) ones, but they found the  $^3A''$  state to be slightly nonplanar. They also reported the triplet state to be lower in energy, by  $7050 \text{ cm}^{-1}$  at the HF/6-311 + + G\*\* level and by  $1236 \text{ cm}^{-1}$  at the CID/6-311 + + G\*\*//HF/6-311 + + G\*\* level.

## 6. Conclusions

The RCCSD(T) method and correlation consistent basis sets were used to determine the structures and other properties of  $C_nH$  radicals for  $n = 2-7$ . In general, predicted valence-correlation values of the rotational constants  $B_e$  were within 100 MHz of experimental or astronomical  $B_0$  values; adding a correction for core and core–valence contraction improves the agreement substantially. The predicted  $^2\Sigma^+ - ^2\Pi$  state separation of  $C_2H$  at the RCCSD(T) level of theory is in good agreement with values determined using multireference methods and with

other theoretical results. In the estimated complete basis set limit, the ground states of  $C_2H$  and  $C_4H$  were found to be of  $^2\Sigma^+$  symmetry and lie 3415 and  $72 \text{ cm}^{-1}$  below their respective  $^2\Pi$  states. The  $^2\Pi$  ground state of  $C_6H$  lies  $895 \text{ cm}^{-1}$  below the  $^2\Sigma^+$  state (RCCSD(T)/cc-pVTZ).

The electron affinities of  $C_2H$  and  $C_3H$  were determined to be 2.964 and 1.825 eV, respectively, which agree well with the experimental values of  $2.969 \pm 0.006$  and  $1.858 \pm 0.023$  eV. Although  $C_2H^-$  is linear,  $C_3H^-$  is not: its ground state is a planar  $^1A'$  state. A  $^3A''$  state lies only  $481 \text{ cm}^{-1}$  higher in energy.

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## References

- [1] D.L. Cooper and S.C. Murphy, *Astrophys. J.* 333 (1988) 482.
- [2] F. Pauzat and Y. Ellinger, *Astron. Astrophys.* 216 (1989) 305.
- [3] F. Pauzat, Y. Ellinger and A.D. McLean, *Astrophys. J.* 369 (1991) L13.
- [4] K.I. Dismuke, W.R.M. Graham and W. Weltner Jr., *J. Mol. Spectry.* 57 (1975) 127.
- [5] C.A. Gottlieb, E.W. Gottlieb, P. Thaddeus and H. Kawamura, *Astrophys. J.* 275 (1983) 916.
- [6] L.N. Shen, T.J. Doyle and W.R.M. Graham, *J. Chem. Phys.* 93 (1990) 1597.
- [7] M.C. McCarthy, C.A. Gottlieb, P. Thaddeus, M. Horn and P. Botschwina, *J. Chem. Phys.*, in press.
- [8] J. Natterer and W. Koch, *Mol. Phys.* 84 (1995) 691.
- [9] S. Dua, J.H. Bowie and J.C. Sheldon, *J. Chem. Soc. Perkin Trans. II* (1994) 543.
- [10] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [11] R.A. Kendall, T.H. Dunning Jr. and R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [12] D.E. Woon and T.H. Dunning Jr., *J. Chem. Phys.*, in press.
- [13] D.E. Woon and T.H. Dunning Jr., *J. Chem. Phys.* 99 (1993) 1914.

- [14] K.A. Peterson, R.A. Kendall and T.H. Dunning Jr., *J. Chem. Phys.* 99 (1993) 1930.
- [15] K.A. Peterson and T.H. Dunning Jr., *J. Chem. Phys.* 99 (1993) 9790.
- [16] K.A. Peterson, D.E. Woon and T.H. Dunning Jr., *J. Chem. Phys.* 100 (1994) 7410.
- [17] D.E. Woon and T.H. Dunning Jr., *J. Chem. Phys.* 101 (1994) 8877.
- [18] K.A. Peterson and T.H. Dunning Jr., *J. Chem. Phys.* 102 (1995) 2032.
- [19] M.J.O. Deegan and P.J. Knowles, *Chem. Phys. Letters* 227 (1994) 321, and references therein.
- [20] H.-J. Werner and P.J. Knowles, *J. Chem. Phys.* 89 (1988) 5803.
- [21] H.-J. Werner and P.J. Knowles, *J. Chem. Phys.* 82 (1985) 5053.
- [22] S.R. Langhoff and E.R. Davidson, *Intern. J. Quantum Chem.* 8 (1974) 61.
- [23] K.A. Peterson, unpublished results.
- [24] M. Mladwnović, S. Schamtz and P. Botschwina, *J. Chem. Phys.* 101 (1994) 5891.
- [25] D.E. Woon, submitted for publication.
- [26] W.P. Kraemer, B.O. Roos, P.R. Bunker and P. Jensen, *J. Mol. Spectry.* 120 (1986) 236.
- [27] A.G. Koures and L.B. Harding, *J. Phys. Chem.* 95 (1991) 1035.
- [28] H. Thümmel, M. Perić, S.D. Peyerimhoff and R.J. Buenker, *Z. Physik D* 13 (1989) 307.
- [29] M. Perić, S.D. Peyerimhoff and R.J. Buenker, *Z. Physik D* 24 (1992) 177.
- [30] K.A. Peterson, *J. Chem. Phys.* 102 (1995) 262.
- [31] K.M. Ervin and W.C. Lineberger, *J. Chem. Phys.* 95 (1991) 1167.
- [32] E.G. Lima and S. Canuto, *Intern. J. Quantum Chem. Quantum Chem Symp.* 22 (1988) 199.
- [33] J.M. Oakes and G.B. Ellison, *Tetrahedron* 42 (1986) 6263.